TRACE METAL CONCENTRATION AND ANALYSIS

OF NATURAL WATERS

A Report to the

GREAT LAKES RESEARCH DIVISION

Institute of Science and Technology

UNIVERSITY OF MICHIGAN

by

Nelson W. Hovey

1968

PREFACE

The untimely death of Dr. Nelson W. Hovey on July 10, 1968 terminated the work of over ten months of research for the Great Lakes Research Division. As a good scientist, Dr. Hovey kept very careful records of his work. It seemed such a waste simply to abandon the results, so I volunteered to undertake the task of writing a report on the project. I'm sure this is not as complete a document as he would have submitted but I hope it will be of some value to those interested in the field and will encourage someone to continue this line of work.

Dr. Hovey thoroughly enjoyed his association with those he came to know at the Division and on many occasions expressed his admiration for the Director, Dr. David C. Chandler, and appreciation for the cooperation of Mrs. Margaret N. Everett, Administrative Assistant.

On his behalf I also would like to acknowledge the help and cooperation of several of the faculty of the College of Engineering of the University of Toledo: Dean Otto Zmeskal, Associate Dean Ernest Weaver, Professors Clyde Balch and Edwin Saxer, and especially of Dr. Norman R. Sedlander whose laboratory he shared. The assistance of Mrs. Viola Polson of the Chemistry Department Stockroom was invaluable in providing items of equipment for outfitting the laboratory.

I respectfully submit this report in memory of a respected teacher and valued friend and colleague of many years.

Albertine Krohn
Professor of Chemistry
University of Toledo

TABLE OF CONTENTS

Page

I. PRELIMINARY WORK

The first two months (September and October, 1967) with Great Lakes Research Division were spent on library work. At first this was directed toward the chemistry of phosphorus and, to a lesser extent, of carbon in lake waters. When it bacame evident that both of the new men joining the Division had considerable experience with phosphate determination, this was discontinued. Bibliography cards for this and later literature search are submitted separately.

During the latter part of October it bacame apparent that laboratory space at the University of Michigan was at a premium. Arrangements were made with the College of Engineering of the University of Toledo to use laboratory space in the Engineering-Science Building on the Toledo campus. Equipment was borrowed from the Division laboratory, the University of Toledo Chemistry Department and the College of Engineering. Additional items were ordered as needed.

All equipment and chemicals were listed in a detailed inventory which continually was kept up to date. It was decided to study methods for the concentration and determination of certain trace elements in natural waters. A good choice seemed to be elements 25-30: manganese, iron, cobalt, nickel, copper and zinc.

November and December were devoted to getting the Toledo laboratory outfitted for ion exchange and spectrophotometric analysis for the selected trace elements. Contact with the Division was maintained by weekly

trips to Ann Arbor for staff meetings and seminars. During this period some preliminary work was done on Lake Erie water collected by Mr. Robert Henderson of the City of Toledo Division of Water during the month of December. This composite sample had passed through activated carbon at the low service pumping station. This proved to be unsatisfactory due to suspended carbon and the probability that the carbon had removed the trace elements. However, a number of determinations were made on this water after filtration through ordinary filter paper followed by millipore filtration. The Hach laboratory kit was used. Filtered water from Columbia Lake, Michigan also was tested. Attempts were made to evaporate water samples from these lakes in order to concentrate the elements and bring them into a range for qualitative analysis by the methods given in "Qualitative Analysis," N. W. Hovey and A. Krohn, Sernoll, Inc., Iowa City (1966). No really positive test was obtained for any of the trace elements.

January brought a sample of Lake Michigan water obtained by the C. & O. Ferry from Ludington to Milwaukee. This was analyzed using the Hach Laboratory. Data on these and on tap water are recorded in Part II of this report.

During February the analytical methods to be used were selected and the necessary chemicals and glassware ordered. The Spectronic 20 spectrophotometer was put into use and several preliminary runs were attempted.

The preliminary work continued into March. This work attempted to

establish the detection limit and practical lower limit for analysis of each of the elements. The data are presented in this report under the specific element determined. A procedure for concentration of lake water by ion exchange and for the spectrophotometric analysis for transition type metals was developed. This is given on page 35.

The trace metal analysis work continued through June. The results are recorded in Parts III and IV. Additional samples of water from Lake Erie and Lake Michigan were analyzed and these results are reported in Part II.

II.   GENERAL WATER ANALYSIS

A. Lake Erie Water

Collection: Raw water intake, Collins Park filtration plant of

the City of Toledo; 18 feet of water, 10 feet below the

surface. One hundred milliliters per day of composite

hourly samples per month. Kept in polyethylene bottle at

room temperature until transferred to refrigerator at 4.0°

at the University of Toledo.

Previous Treatment: Activated carbon added at low service pump-

ing station.

Appearance: Turbid; particles of carbon floating in sample.

Filtration: December composite through Whatman #5 (sample still

turbid after filtration). March, April and May composites

filtered through 0.8 micron millipore filter. (Slow process

as filters clog readily.)

Analysis: pH by "Analytical Instruments" pH meter. Other deter-

minations by Hach Direct Reading-Engineer's Laboratory Anal-

ysis Kit.

Results: See Table 1.

B. Lake Michigan Water

Collection: C. & O. Ferry, 17 1/2 feet below the surface through

clean intake. Latitude 43.8 N, longitude 86.4 W. Sample in

10 gallon polyethylene bottle.

Previous Treatment: None.

Appearance: Clear.

Filtration: None.

Analysis: As for Lake Erie Water.

Results: See Table 2.

C. Columbia Lake Water

Collection: Just below surface at end of dock.

Previous Treatment: None.

Appearance: Slightly turbid.

Filtration: Through 0.8 micron millipore filter.

Analysis: As for Lake Erie Water.

Results: See Table 3.

D. Tap Water

Collection: From tap in Engineering-Science Room 1006; allowed to

flow until temperature constant at 6° C.

Previous Treatment: None.

Appearance: Clear.

Filtration: None.

Analysis: As for Lake Erie Water

Results: See Table 3.

TABLE 1

ANALYSIS OF LAKE ERIE WATER

	Conc. as p.p.m.			
	Dec.	March	April	May
Alkalinity	85	85	90	95
Chloride	22.5	27.5	25	25
Copper	0.2	0.08	0.15	0.17
Fluoride	0.22	0.20	0.25	0.25
Hardness (Total)	145	130	130	135
Iron	0.06	0.05	0.08	0.03
Manganese	0.25	0.25	0.23	0.25
Nitrogen ($NO_2^- + NO_3^-$)	1.0	0.62	1.08	1.4
Phosphate (ortho)	0.26	0.22	0.22	0.16
Silica	0.35	0.43	0.40	0.72
Sulfate	40	28	28	37
pH	8.1	8.0	8.0	8.0

TABLE 2

ANALYSIS OF LAKE MICHIGAN WATER

	Conc. as p.p.m.	
	January	April
Alkalinity	110	113
Chloride	10.0	10.0
Copper	0.1	
Fluoride	0.4	0.16
Hardness (Total)	120	130
Iron	0.02	0.03
Manganese	0.00	0.03
Nitrogen ($NO_2^- + NO_3^-$)	0.16	0.19
Phosphate (ortho)	0.07	0.06
Silica	1.7	1.72
Sulfate	20.0	18.0
pH	8.2	7.9

TABLE 3

ANALYSIS OF COLUMBIA LAKE AND TAP WATER

	Conc. as p.p.m.	
	Columbia Lake	Tap
Alkalinity	170	20
Chloride	17.5	22.5
Copper	0.3	0.35
Fluoride	0.25	1.25
Hardness (Total)	245	70
Iron	0.03	0.1
Manganese	0.05	0.1
Nitrogen (NO_2^- + NO_3^-)		6
Phosphate (ortho)	0.16	
Silica	0.9	
Sulfate	92	28
pH	8.35	9.4

III. TRACE METAL ANALYSIS METHODS

A. COBALT

REFERENCE: E. B. Sandell, "Colorimetric Determination of Traces

of Metals," Third Edition, Interscience Publishers,

New York (1959). Procedure A, page 419.

REAGENTS: Nitroso-R salt (sodium 1 nitroso-2-hydroxynaphthalene-

3-6-disulfonate). Use 200 mg of the salt in 100 ml

(0.2%), store in plastic or glass, keep away from light;

stable for months.

Standard cobalt solution; 1 mg/ml = 1 ppm.

Nitric acid (conc.), hydrochloric acid (6 N)

Sodium acetate (solid)

Bromcresol green indicator solution, buffer at pH 5.5.

GLASSWARE: 3 250-ml beakers, 3 10-ml volumetric flasks, medicine

droppers, spot plate.

APPARATUS: Steam bath, Spectronic 20.

PROCEDURE: Evaporate the solution containing 1-10 micrograms of

cobalt (usually either 10 or 25 ml) almost to dryness in a 50-ml

Erlenmeyer flask. Add 1 (2) ml of concentrated nitric acid to

oxidize iron and continue the evaporation just to dryness. Take up the residue in 5 (10) ml of water, 5 (10) drops 1:1 hydrochloric acid and 5 (10) drops 1:10 nitric acid. Boil if necessary to dissolve all solid material. Add exactly 0.5 (1.0) ml of nitroso-R salt solution and 0.6 (1.2) grams of anhydrous sodium acetate. The pH should be about 5.5 and this may be checked with bromcresol green indicator and pH 5.5 buffer. Boil for one minute, add 1.0 (2.0) ml of conc. nitric acid and boil again for one minute. Cool to room temperature in the dark, dilute to 10 (25) ml in a volumetric flask. Measure the absorbance at 420 millimicrons.

SUMMARY OF PRELIMINARY DETERMINATIONS: A standard containing 1 µg/ml was prepared. Since this was stored in glass, 3 drops of 2N HCl were added to the 500 ml prepared to prevent "plating out" on the glass bottle. The evaporation was done in a small casserole and there may have been some loss of solution. The results of these preliminary determinations are given on page 11.

CONCLUSIONS: The limit of detection is about 50 µg/ml. The limit for reasonably accurate determinations is about 100 µg/ml. The procedure is reasonably satisfactory except for the considerable boiling required. If trace element work is continued by spectrophotometric methods, a procedure described on page 422 of Sandell might be tried.

SUMMARY OF PRELIMINARY COBALT DETERMINATIONS

Ml. std. used	conc. μg/l	% Trans.	Absorbance	Absorbance corr. for blank
Blank	0	29.2	0.535	
0.25	25	33.2	0.479	negative
0.50	50	25.9	0.587	0.052
0.75	75	25.1	0.600	0.065
1.00	100	19.5	0.710	0.165
2.00	200	15.3	0.817	0.272
3.00	300	11.3	0.947	0.402
4.00	400	9.0	1.046	0.505
5.00	500	6.8	1.167	0.622

CALIBRATION CURVE: After considerable experience with the procedure and its applications to the analysis of natural waters, a calibration curve was constructed. The high purity water used in preparing the standards and for the blank was distilled water which was then passed through an Illco-way Research Model ion exchanger. The data are given below and the curve on page 13.

DATA FOR CALIBRATION CURVE

ml standard/10 ml soln.	Conc. in µg/l	Corrected Absorbance
Blank		0.565
0.1	10	0.005
0.5	50	0.022
1.0	100	0.130
1.5	150	0.197

COBALT
CALIBRATION CURVE

Concentration of Co^{2+} in µg/liter

Absorbance at 420 mµ

0.200
0.100

50
100
150
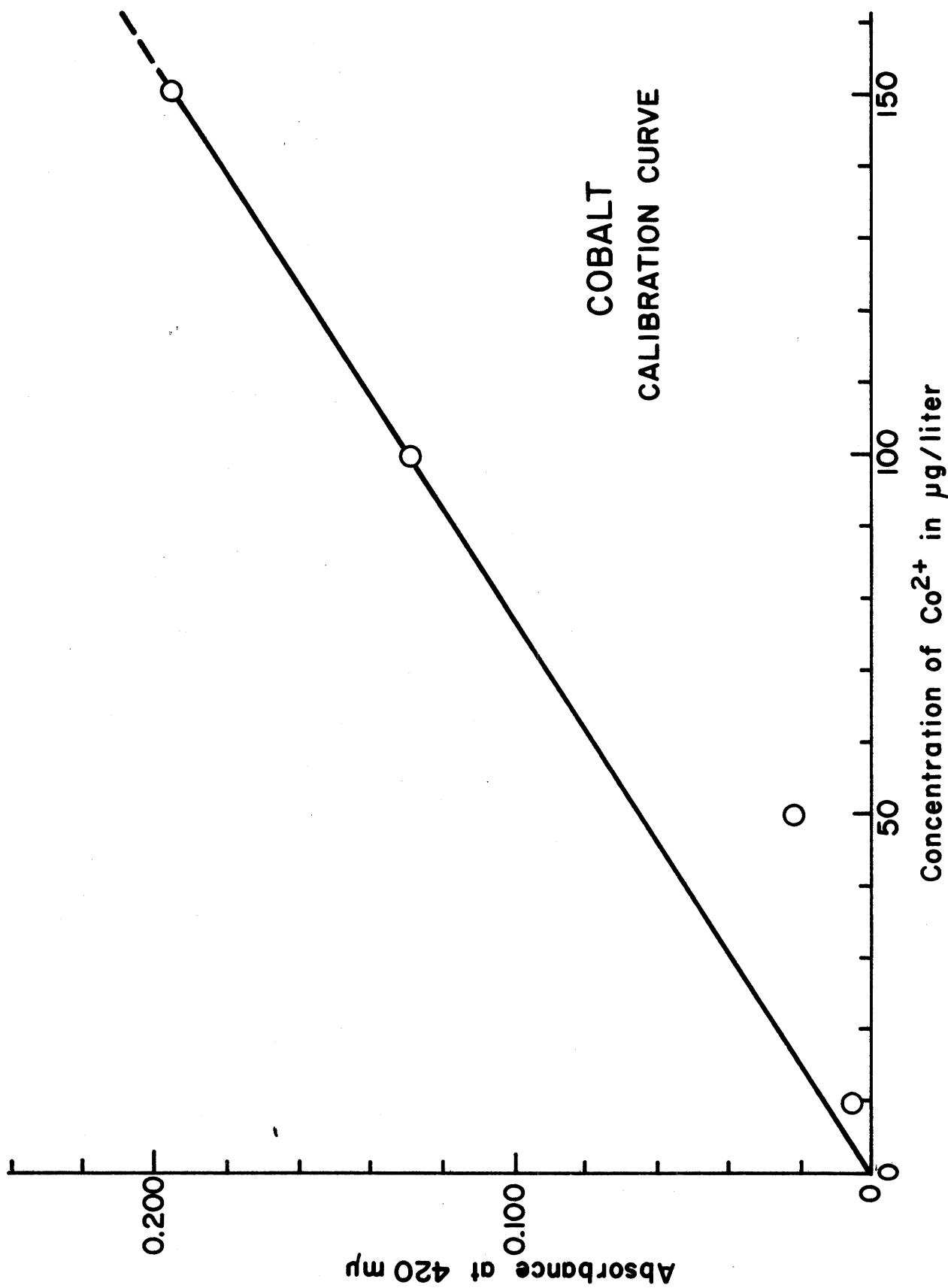
B. COPPER

REFERENCE: Sandell, Procedure II, page 449.

REAGENTS: Sodium diethyldithiocarbamate, 0.1% solution, 100 mg

in 100 ml, stable for 1 week, store in amber bottle.

Disodium ethylenediaminetetraacetate, 10 g in 100 ml.

Chloroform

Ammonium citrate - Mix 210 ml of concentrated ammonia

with 100 ml of water and add 200 g of citric acid in

small portions while stirring and cooling. Make the

solution slightly ammoniacal, add a little sodium di-

ethyldithiocarbamate and extract traces of copper with

chloroform. Dilute to 500 ml.

Cresol red, 0.01%

Ammonium hydroxide, concentrated.

GLASSWARE: 3 separatory funnels, 3 25-ml volumetric flasks, 10-ml

graduated cylinder, beakers, flasks, stirring rods.

APPARATUS: Spectronic 20.

PROCEDURE: Zero the Spectronic 20 using chloroform. The sample may

have a volume of 10-20 ml and up to 40 micrograms of Cu. Add 5 ml

of ammonium citrate, 10 ml of the sodium EDTA and 5 drops of 0.01%

cresol red indicator to the sample solution, followed by concentra-
ted ammonia until the indicator shows its alkaline color (pH = 8.5).
Transfer the solution to a separatory funnel and wash the flask
twice into the funnel with 5 ml portions of water. Add 5 ml of
sodium diethyldithiocarbamate solution and shake vigorously for
1-2 minutes with 10 ml of chloroform. Run the chloroform extract
into a 25-ml volumetric flask and extract twice more with 5 ml
portions of chloroform. Dilute the combined extracts to 25 ml
with chloroform. Filter if necessary directly into the absorption
cell. Measure the absorbance at 435 millimicrons.

SUMMARY OF PRELIMINARY DETERMINATIONS: The secondary standard copper
solution contained 5 ppb of copper and 5 drops of 2N HCl per liter.
The third extraction was omitted in the runs with 5 and 10 micro-
grams of copper. The results are given on page 16.

CONCLUSIONS: The limit of detection is about 20 micrograms per
liter and the limit of reasonably accurate determination is about
100 micrograms per liter. The procedure given above appears to be
entirely satisfactory.

SUMMARY OF PRELIMINARY COPPER DETERMINATIONS

Solution used	Conc. µg/1	% Trans.	Absorbance
Deionized water	?	99.9	0.001
Lake Michigan	?	99.8	0.001
Columbia Lake	?	Neg.	
Tap water	?	97.5	0.001
1 ml std.	200	85.6	0.067
2 ml std.	400	71.5	0.146
5 ml std.	1000	41.0	0.390

CALIBRATION CURVE: Data for the calibration curve are given below and the curve on page 17.

DATA FOR CALIBRATION CURVE

ml standard/10 ml soln.	Conc. in µg/1	Corrected Absorbance
Blank		0.010
0.5	100	0.041
1.0	200	0.080
1.5	300	0.120
2.0	400	0.164

COPPER CALIBRATION CURVE

Concentration of Cu^{2+} in µg / liter

Absorbance at 435 mµ

0.200

0.100

300

150
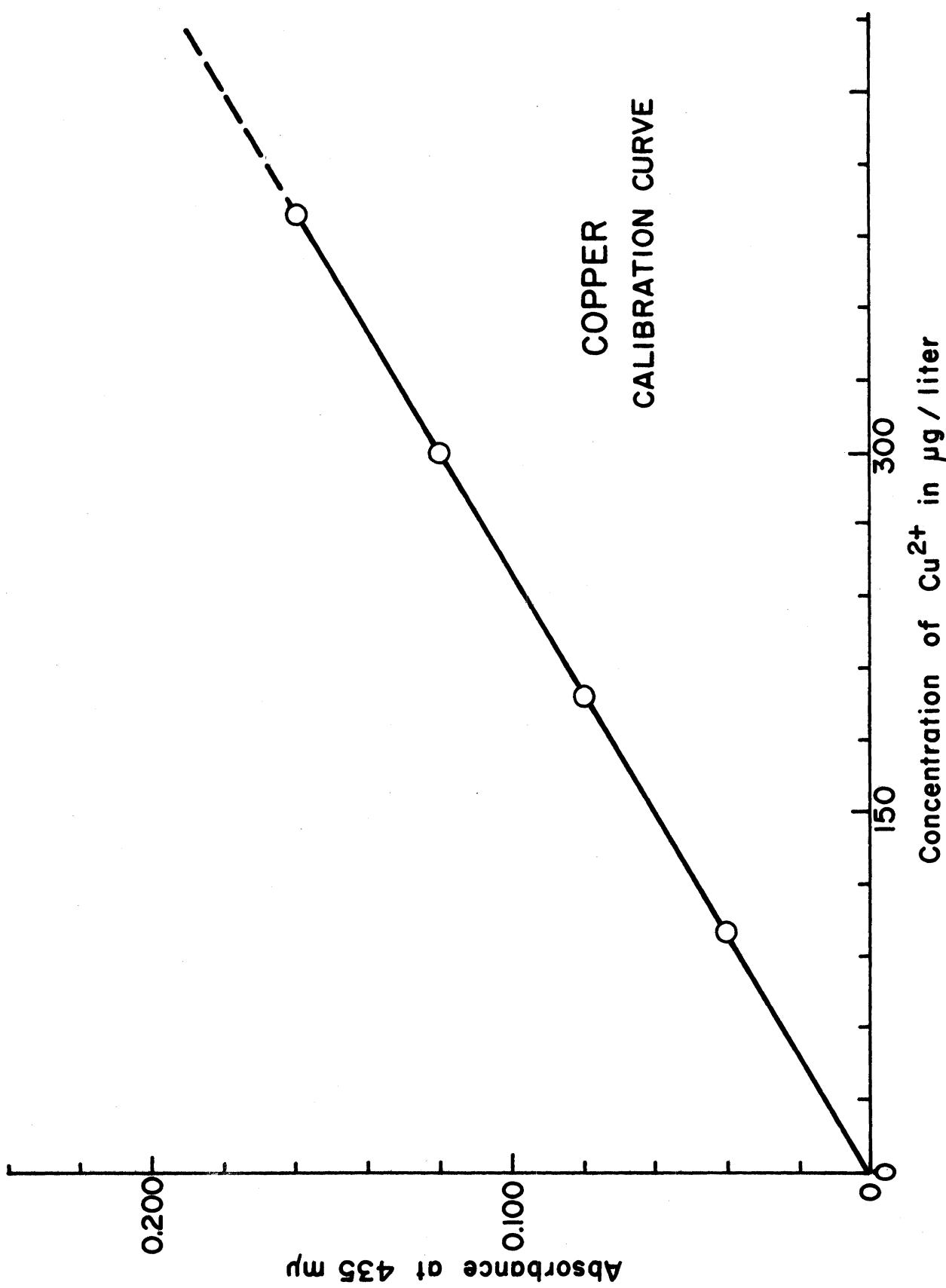
C. IRON

REFERENCE: Sandell, Procedure B, page 548.

REAGENTS: Hydroxylamine hydrochloride (10%).

Sodium acetate (10%)

4, 7-diphenyl-1, 10 phenanthroline (0.001 M). (33 mg

in 100 ml of a 1:1 volume mixture of isoamyl and ethyl

alcohols.)

Ethyl alcohol

Isoamyl alcohol

GLASSWARE: 3 separatory funnels, 3 25-ml volumetric flasks.

APPARATUS: Spectronic 20.

PROCEDURE: To 25 ml of sample (0.1 - 10 ppm Fe) add 5 ml of 10%
hydroxylamine hydrochloride solution and 10 ml of 10 % sodium
acetate. Add 10 ml of the phenanthroline, 15 ml of isoamyl alcohol
and shake well. Allow the phases to separate for 5 minutes, drain
off the aqueous phase, and transfer the alcohol to a 25-ml volumet-
ric flask. Rinse the separatory funnel with a few ml of ethyl
alcohol and make up to volume with it. Obtain the absorbance of
the clear mixed solution at 533 millimicrons.

SUMMARY OF PRELIMINARY DETERMINATIONS: Extreme care must be used
to avoid contamination of the reagent. A summary of the data is
given below.

SUMMARY OF PRELIMINARY IRON DETERMINATIONS

Solution used	Conc. µg/l	% Trans.	Corr. Absorbance
Deionized water	?	86.3	0.063
Lake Michigan	?	86.0	0.002
0.1 ml std.	20	82.9	0.017
0.5 ml std.	100	61.8	0.157
1.0 ml std.	200	45.5	0.279
2.0 ml std.	400	21.2	0.617

CONCLUSIONS: The limit of detection is about 10 micrograms per
liter and the limit for reasonably accurate determination is about
30 micrograms per liter. A slight pink color appears upon adding
isoamyl alcohol to the 4,7-diphenyl-1,10-phenanthroline. Except
for this, the method appears very satisfactory and relatively sim-
ple.

CALIBRATION CURVE: The Spectronic 20 was zeroed with 8 ml isoamyl
+ 2 ml ethyl alcohol mixture. The blank does not seem excessive
in relation to the very high absorbances observed with dilute

solutions of the standard. Data for the calibration curve are
given below and the curve is on page 21.

DATA FOR CALIBRATION CURVE

ml standard/10 ml soln.	Conc. in µg/l	Corrected Absorbance
Blank		0.079
0.1	100	0.053
0.5	500	0.393
1.0	1000	0.807
1.5	1500	1.222

IRON
CALIBRATION CURVE

Concentration of Fe^{3+} in µg/liter

Absorbance at 533 mµ

1.000

0.500
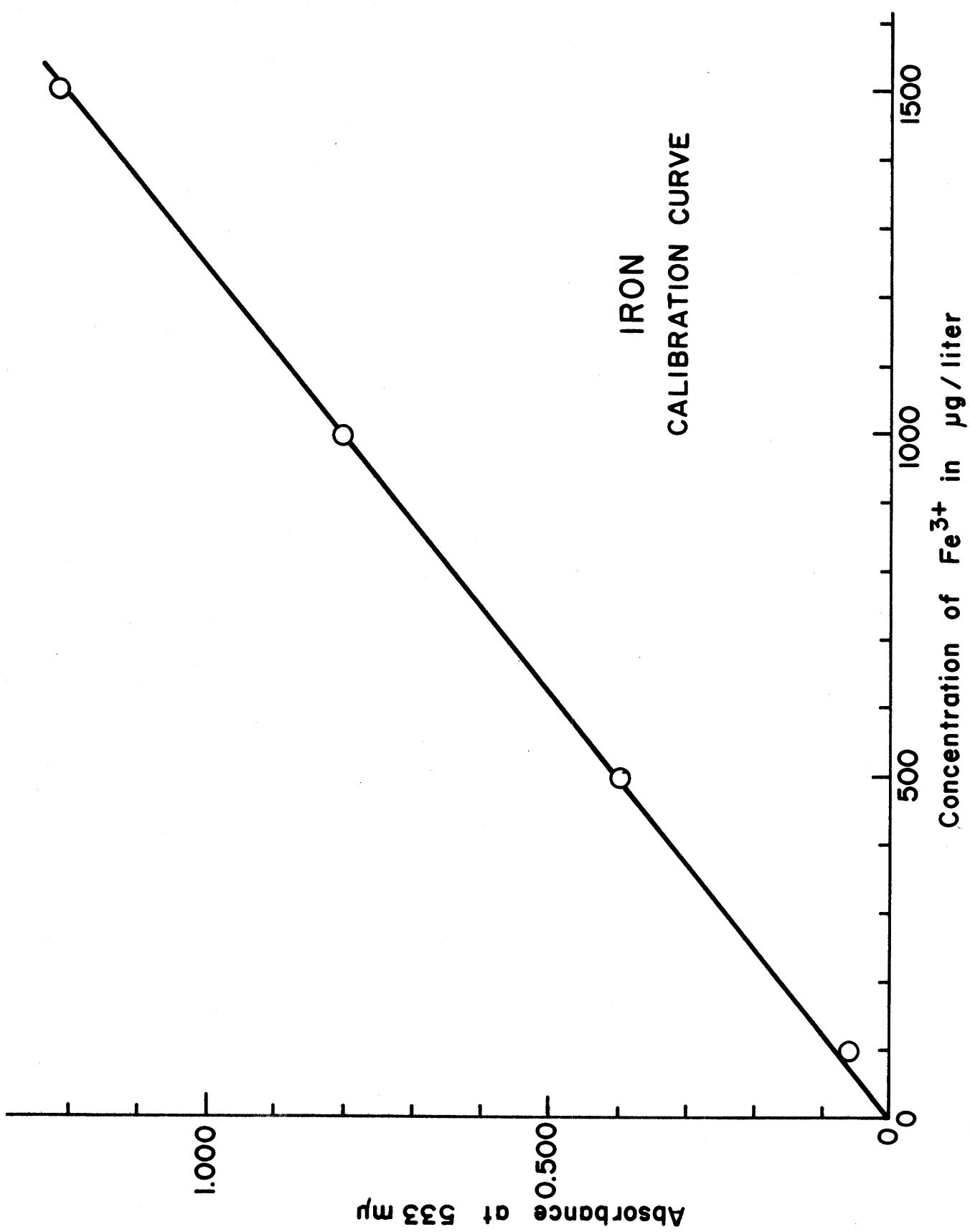
D. MANGANESE

REFERENCE: "Standard Methods for the Examination of Water and
Wastewater," 12th Edition, American Public Health
Association, New York (1965), Procedure A, page 173;
Sandell, page 612.

REAGENTS: Special reagent - Dissolve 75 g mercuric sulfate in
400 ml conc. nitric acid and 200 ml water. Add 200
ml 85% phosphoric acid and 0.035 g silver nitrate, and
dilute the cooled solution to 1 liter.
Ammonium persulfate - solid.

APPARATUS: Spectronic 20.

PROCEDURE: Add 5 ml of the special reagent to the sample solution
(0.005 to 5 mg of Mn). Dilute to about 90 ml, add 1 g of ammonium
persulfate, and bring to boiling in about 2 minutes over a flame.
Remove the flask from the flame and cool under the tap after stand-
ing for 1 minute. Dilute to 100 ml and obtain the absorbance at
525 millimicrons unless considerable chromium is present, in which
case measure at 545 millimicrons.

SUMMARY OF PRELIMINARY DETERMINATIONS: The final volume was 100
ml ±3 ml. Data are given on page 23.

SUMMARY OF PRELIMINARY MANGANESE DETERMINATIONS

Solution used	Conc. µg/l	% Trans.	Absorbance
Lake Michigan	?	off scale	off scale
0.5 ml std.	50	off scale	off scale
1.0	100	98.8	0.005
2.0	200	97.2	0.011
3.0	300	96.5	0.015
4.0	400	94.9	0.021
5.0	500	90.6	0.042
10.0	1000	83.5	0.083

CONCLUSIONS: The limit for detection is about 100 µg/liter. The limit for accurate determination is about 500 µg/liter. The method lacks the necessary sensitivity for trace analysis. Alternate methods do not appear very attractive although some are more sensitive. It might be possible to use a larger sample and/or a smaller final volume. (See page 40.)

CALIBRATION CURVE: A 10.0 ml sample was used and a first volume of 25.00 ml instead of the 100 ml given in Sandell. Data for the calibration curve are given on page 24 and the curve is on page 25.

DATA FOR CALIBRATION CURVE

ml standard/10 ml soln.	Conc. in µg/l	Absorbance
0.5	200	0.011
1.0	400	0.027
1.5	600	0.046
2.0	800	0.060

MANGANESE
CALIBRATION CURVE
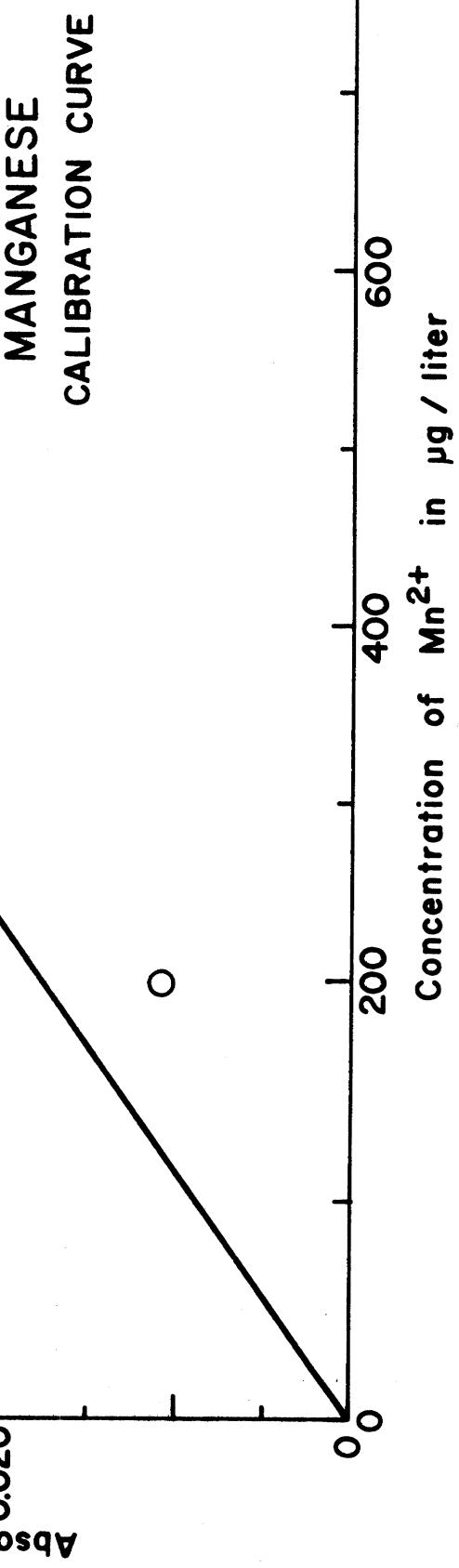
E. NICKEL

    REFERENCE: Sandell, Alternate Procedure A, page 672.

    REAGENTS: Sodium citrate (20%)

                    Hydroxylamine hydrochloride (10%)

                    Dimethylglyoxime (1% in alcohol)

                    Ammonium hydroxide (conc.)

                    Chloroform

                    Ammonium hydroxide (1:50)

                    Hydrochloric acid (0.5 M)

                    Dimethylglyoxime (2.5% in 1M sodium hydroxide)

                    Sodium hydroxide (10 M)

                    Ammonium persulfate (10%)

                    Phenolphthalein indicator

    GLASSWARE: 3 250-ml separatory funnels (graduated), 3 125-ml separatory funnels, 3 60-ml separatory funnels, 3 25-ml volumetric flasks.

    APPARATUS: Spectronic 20

    PROCEDURE: Pipet 25 ml of sample into each of 2 125-ml separatory funnels and 25 ml of high purity water into a third. To each add 10 ml of 20% sodium citrate, 2 ml of freshly prepared hydroxylamine hydrochloride, 2 ml of 1% alcoholic dimethylglyoxime, and 2 drops

phenolphthalein. Neutralize with conc. ammonium hydroxide and add
3 drops in excess. Dilute to 60 ml and shake for 2 minutes with
20 ml of chloroform. Separate the phases transferring the chloro-
form layer to 60-ml funnels. Empty the aqueous phase through the
tops of the 125-ml funnels and discard. Rinse with pure water.
Shake the chloroform solutions with 10 ml of 1:50 ammonium hydrox-
ide for 1 minute. Transfer the chloroform layer to the original
125-ml funnels. Drain and water rinse the 60-ml funnels. Shake
the chloroform solution in the 125-ml funnels with 10 ml of 1:50
ammonium hydroxide for 1 minute. Transfer the chloroform layer to
the rinsed 60-ml funnels. Add 5 ml of 1M HCl and shake for 1 min-
ute. Separate the phases, discarding the chloroform.

To the acid solution in the funnels, add 1 ml 10M NaOH, 1 ml of
2.5% dimethylglyoxime in 1M NaOH and 6 drops of 10% ammonium per-
sulfate solution. Swirl to mix and transfer to 25-ml volumetric
flasks. Dilute to volume after 10 minutes using high purity water
and rinsing the funnels in the process. Measure the absorbance at
460 millimicrons.

SUMMARY OF PRELIMINARY DETERMINATIONS: The procedure was followed
exactly except that the wash with dilute ammonium hydroxide to re-
move copper was omitted. The recorded runs were made on different
days and do not appear to be consistent. A precipitate appeared
when the alkaline dimethylglyoxime was added to one of the samples

so the amount was cut from 2 ml to 1 ml and this may account for the lower absorbance on the second day (200 and 1200 µg/l samples.)

SUMMARY OF PRELIMINARY NICKEL DETERMINATIONS

Solution used	Conc. µg/l	% Trans.	Absorbance
Pure water	00	94.8	0.024
Lake Michigan	?	98.5	0.006
0.50 ml std.	200	97.4	0.011
1.00 ml std.	400	ppt.	
2.00 ml std.	800	81.8	0.088
3.00 ml std.	1200	84.0	0.076

CONCLUSIONS: The limit of detection is about 50 µg/liter and the limit for reasonably accurate determination is about 100 µg/liter. The procedure is very lengthy. The results are not very consistent partly due to a rather great change in the absorbance of the final solutions with time. However, the method appears as good as any available.

CALIBRATION CURVE: The first set of spectrophotometric readings were taken after 10 minutes in each case and the second set after about 15 minutes (5 additional minutes). Data are given on page 29 and the curve appears on page 30.

DATA FOR CALIBRATION CURVE

ml. std.	Conc. in µg/l	Corr. Absorbance	Corr. Absorbance
Blank	0	0.011	0.008
1.00	400	0.093	0.090
2.00	800	0.308	0.378
3.00	1200	0.186	0.458
4.00	1600	0.164	0.268
5.00	2000	0.598	0.858

NICKEL
CALIBRATION CURVE
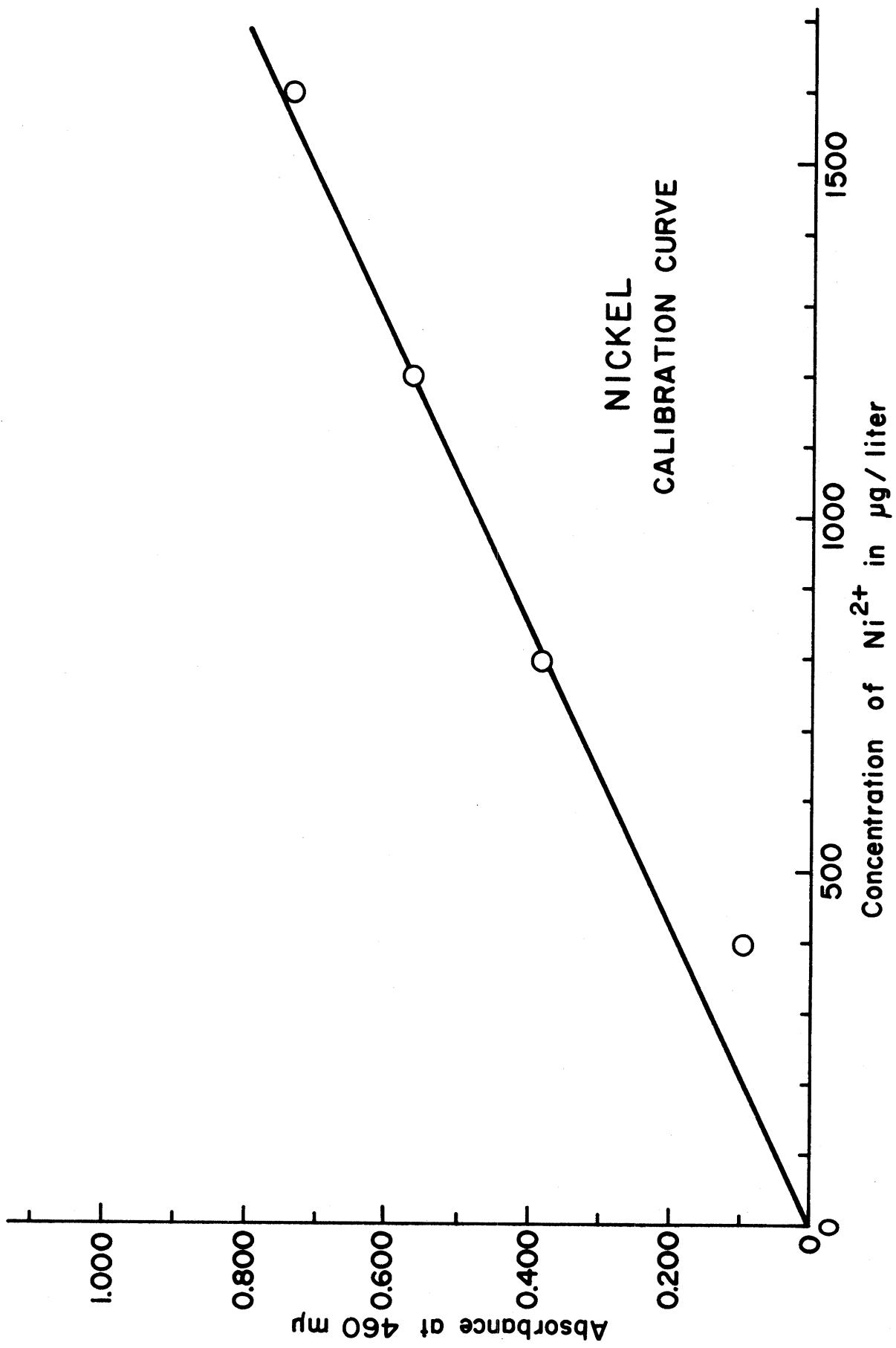
F. ZINC

REFERENCE: Standard Methods, pp. 318-20; Sandell, page 951.

REAGENTS: All should be zinc free.

Hydrochloric acid, 2N

Sodium acetate, 2N (68 g $NaC_2H_3O_2.3H_2O$ in final volume of 250 ml)

Acetate buffer - mix equal volumes of 1 + 7 acetic acid and 2N sodium acetate.

Sodium thiosulfate - Dissolve 25 g $Na_2S_2O_3.5H_2O$ in 100 ml water.

Dithizone (I) - Dissolve 0.10 g diphenylthiocarbazone in 1 liter of carbon tetrachloride. Store in brown glass in the refrigerator.

Dithizone (II) - Dilute dithizone 1:10 using carbon tetrachloride. Store in brown bottle in a refrigerator. Good for several weeks.

GLASSWARE: 60-ml separatory funnels, pipets, beakers.

APPARATUS: Spectronic 20.

PROCEDURE: Adjust the pH of the sample to between 2 and 3 with HCl first removing excess HCl if necessary by evaporation in a silica dish. Transfer 10 ml of the sample to a 60-ml separatory funnel,

add 5 ml of acetate buffer and 1.0 ml sodium thiosulfate and mix.
The pH should be between 4 and 5.5 at this point. Add 10.0 ml of
dithizone (II), stopper and shake vigorously for 4.0 minutes.
Transfer to clean, dry large size colorimeter tubes and measure
the absorbance at 535 millimicrons.

SUMMARY OF PRELIMINARY DETERMINATIONS: The blank was used to set
the spectrophotometer at 100% transmittance. The data appear below.

SUMMARY OF PRELIMINARY ZINC DETERMINATIONS

Solution used	Conc. µg/l	% Trans.	Absorbance
Lake Michigan	?	100+	
Tap water	?	100	
0.1 ml std.	100	59.0	0.240
0.2 ml std.	200	35.0	0.455
0.3 ml std.	300	18.8	0.730
0.4 ml std.	400	12.0	0.920
0.5 ml std.	500	5.2	1.30

CONCLUSIONS: The limit of detection is about 1 µg/liter. Because
of the extreme sensitivity of the determination care must be taken
to use zinc-free water and reagents or to extract the zinc impurities
with dithizone. The procedure is relatively simple and appears to
be entirely satisfactory.

CALIBRATION CURVE: Data for the calibration curve are given below

and the curve is shown on page 34.

DATA FOR CALIBRATION CURVE

ml standard/10 ml soln.	Conc. in μg/l	Absorbance
0.1	50	0.095
0.3	150	0.397
0.5	250	0.569
0.7	350	0.824

ZINC
CALIBRATION CURVE

Concentration of Zn^{2+} in μg / liter

Absorbance at 535 mμ
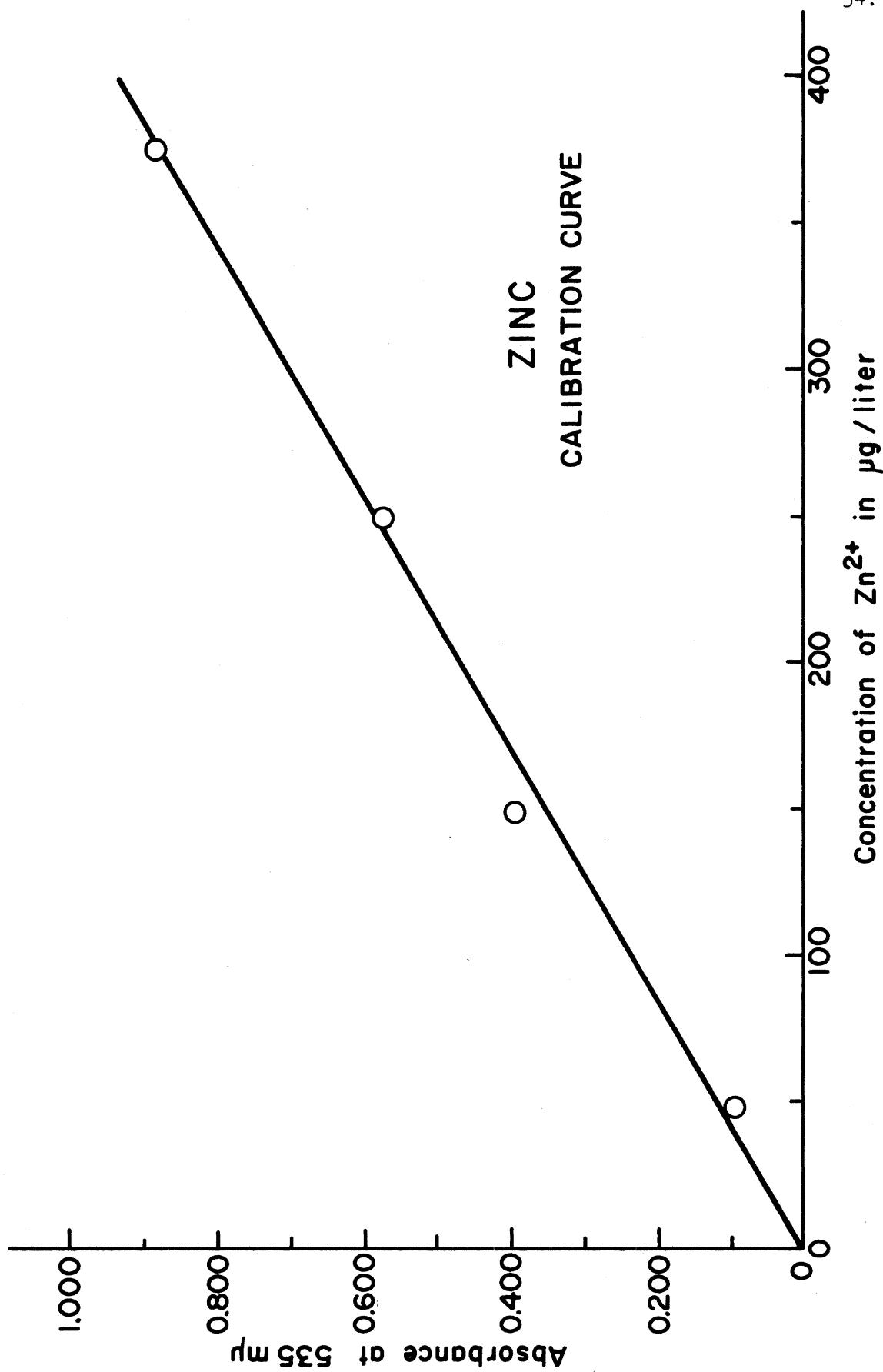
IV. DATA ON WATER ANALYSIS

A. "Spiked" Lake Michigan Water

1. Preparation of the ion exchange column.

Place about 20 g of strongly acid cation exchange resin (Dowex 50W-X8 or Amberlite-IR 120) in an Erlenmeyer flask, cover with water and let stand overnight. Pour off the water and any fines in the resin. Add 4N HCl, shake and allow to stand. Wash with large portions of water. Pour on 1M NaOH, pour off after 2-4 hours and wash several times with water. Finally pour 20-50 ml of 1-2N HCl on to the resin, mix with water and transfer to the column which has previously been filled with water. Pass 2-4N HCl through the column to transfer to the hydrogen form. The rate should be 2-4 ml per minute per square centimeter. It will require about 100 ml of 2N acid for 10 grams of resin. Wash with water at 5-6 ml per minute per square centimeter.

Attach the plastic separatory funnel to the top of the column and a plastic delivery tube with screw clamp to the outlet capillary tube.

2. Preparation of "Spiked" Lake Michigan Water

To a 2-liter volumetric flask, add 4 ml each of standard copper and zinc solutions and 2 ml each of the iron and manganese standard solutions. Add 10 drops of 2N HCl and dilute to the mark with Lake Michigan water. This solution will contain 10 micrograms per liter

of each of the four ions plus whatever is contained in the Lake Michigan water.

3. Concentration of the Sample.

Adjust the pH of the spiked water to 6.5-7.5 by adding dilute NaOH and checking with a pH meter or a suitable indicator. Run 1000 ml of the spiked water through the column at 10 ml per minute. Wash with pure water to displace the sample. Elute at 1 ml per minute using 20 ml of 2N HCl followed by enough water to give an eluent volume of 100 ml.

4. Analysis.

Run determinations on the spiked Lake Michigan water using unspiked Lake Michigan water as the reagent blank. Also run determinations on the concentrated sample using unspiked Lake Michigan water for the reagent blank. Run a sample of equivalent estimated concentration prepared from the standard.

5. Results.

	Standard		"Spiked" water		After Ion Exchange	
	Abs.	µg/l	Abs.	µg/l	Abs.	µg/l
Copper	0.036	100	0.003	10	0.010	28
Iron	0.101	100	0.058	57	0.040	40
Manganese	0.007	100	0.002	30	0.000	-

B. Lake Michigan Water

1. Preparation of the Sample

Ten liters of the January sample of Lake Michigan water (see page 4) were passed through the cation exchange column. The resin was Dowex 50W-X8, about 26 cm^3 in volume. The column was eluted with 100 ml of 4N HCl. The rate of elution was adjusted within the range 1-2 ml per minute. The column was flushed with 100 ml of high purity water. This 200 ml concentrate was evaporated in a 250-ml silica dish to incipient dryness, taken up in high purity water and diluted to 100 ml. Samples of 10.00 ml each were used in testing for all six metals. The concentration factor was 100:1.

2. Results

	Blank		Standard		Conc. Sample	
	Abs.	µg/l	Abs.	µg/l	Abs.	µg/l
Cobalt	0.430	0	0.076	100	0.061	80
Copper	0.019	0	0.153	400	0.168	440
Iron	0.039	0	0.289	400	0.102	110
Manganese	0.003	0	0.009	120	0.018	200
Nickel	-	0	0.088	1000	0.036	410
Zinc	-	0	1.98	1000	0.452	200

NOTE: Absorbances in this and other following tables are averages of several measurements. For the standard and sample, these have been corrected for the blank.

C. Filtered Lake Erie Water and Filter Extract

1. Preparation of the Sample

Twelve liters of the March composite of Lake Erie water were filtered through an 0.8 micron millipore filter. Six drops of 6N HCl were added to each liter of water, changing the pH from 8 to 3.5. The millipore filters from the above filtration were placed in a flask with about 50 ml of 12N HCl and heated on a hot plate at low temperatures. The filters began to disintegrate in a few hours leaving a yellow solution. This was filtered by suction through Whatman #5 filter paper. The excess HCl was removed by evaporation and the residue taken up in high purity water.

2. Results

	Standard		Filtered Water		Filter Extract	
	Abs.	µg/l	Abs.	µg/l	Abs.	µg/l
Cobalt	0.088	50	neg.	-	0.269	200
Copper	0.073	200	neg.	-	0.040	100
Iron	0.393	500	0.004	3	0.681	880
Manganese	-	-	neg.	-	neg.	-
Nickel	0.088	1000	neg.	-	0.025	280
Zinc	0.229	100	0.020	15	-	-

D. Lake Erie Water Concentrated by Ion Exchange

1. Preparation of the Sample

In order to compare the effectiveness of the two resins, identical ion exchange columns were set up using Dowex 50W-X8 and Chelex 100 (Na^+ form). The latter is a chelating ion exchange resin which is supposed to show an unusually high preference for heavy metal cations. Two liters of millipore filtered Lake Erie water were passed through each resin column using the same flow rate as nearly as possible. Each column was eluted with 100 ml of 4N HCl followed by 100 ml of pure water. These eluents were evaporated to incipient dryness in a silica dish, taken up in high purity water and transferred to a 100-ml volumetric flask. After adjusting the pH to about 4, they were diluted to the mark. This gave a 20:1 concentration of the original lake water.

2. Results

	Dowex		Chelex		Dowex:Chelex Ratio
	Abs.	µg/l	Abs.	µg/l	
Cobalt	0.028	21	0.079	60	0.35:1
Copper	0.039	95	0.018	45	2.1:1
Iron	0.094	120	0.025	45	3.7:1
Manganese	0.009	120	0.025	50	2.4:1
Nickel	0.003	60	0.012	230	0.26:1
Zinc	0.726	320	0.818	350	0.92:1

E. Lake Michigan Water (April Sample)

1. Preparation of the Sample

This study was an attempt to compare the efficiency of methods of concentration of natural waters by evaporation and by ion exchange. Five liters of unfiltered Lake Michigan water collected in April and kept under refrigeration were evaporated to dryness and the organic matter oxidized with concentrated nitric acid to give a white ash. This was taken up in dilute HCl. A white precipitate assumed to be $CaSO_4$ was filtered off and thoroughly washed. The volume was adjusted to 100.0 ml.

Another five liters of the same batch of Lake Michigan water was put through an ion exchange column composed of 3/4 Chelex 100 and 1/4 Dowex 50 at a low rate. This was eluted with 2N HCl. The theoretical concentration factor is 50:1.

A new procedure was used to give a more concentrated solution for the measurement of absorption by manganese. Use 10.00 ml samples in 50-ml Erlenmeyer flasks. Add 5 ml of special reagent, 5 ml high purity water, and 0.5 g ammonium persulfate. Bring to a boil in about two minutes. Let stand one minute, then cool under the tap. Transfer to a 25-ml volumetric flask, dilute to the mark and measure absorbance at 545 millimicrons.

2. Results

	Standard		Evaporation		Exchange	
	Abs.	µg/l	Abs.	µg/l	Abs.	µg/l
Cobalt	0.237	50	0.095	75	0.085	67
Copper	0.027	25	0.022	50	0.022	50
Iron	0.183	30	0.025	45	0.273	350
Manganese	0.026	400	turbid	?	0.008	110
Nickel	0.008	150	0.009	170	0.018	340
Zinc	0.824	350	0.509	225	0.886	375

F. Lake Michigan Water by Double Ion Exchange

1. Preparation of the Sample

Two liters of the April sample of Lake Michigan water were passed through the Dowex 50 column. The column was eluted with 50 ml of 12N HCl followed by 10 ml of water and passed to a second column containing Amberlite IRA 400. The eluent was collected and saved for the nickel determination since no chloro complex is formed. The Amberlite 400 was eluted with 200 ml of high purity water which was then evaporated to dryness and taken up in high purity water. After adjusting the pH to 2-4, the solution was diluted to 50.00 ml. The theoretical concentration factor is 40:1.

2. Results

	Blank		Standard		Sample	
	Abs.	μg/l	Abs.	μg/l	Abs.	μg/l
Cobalt	0.547	0	0.065	50	0.252	192
Copper	0.013	0	0.039	100	0.033	85
Iron	0.036	0	0.405	500	1.384	1700
Nickel	-	-	0.009	170	0.003	60
Zinc	-	-	0.824	350	1.97	845

G. Lake Erie Water (April)

1. Preparation of the Sample

Two liters of the Lake Erie composite for April measured in a
two liter volumetric flask were taken from the 5 gallon carboy with
previous thorough agitation to disperse the insoluble matter (algae
mostly) so that a representative sample would be obtained. Evap-
oration was carried out in a 500-ml long-necked flask using a heat-
ing mantle. The sample was finally carefully transferred to a silica
dish. Repeated evaporation with conc. nitric acid failed to produce
a white residue so heating in a muffle furnace was tried. No means
was available for measuring the temperature but it was estimated
to be 600-700° C.

The residue from ignition was nearly but not completely white.
It was taken up in water (partially soluble), evaporated on a water
bath and again treated with conc. nitric acid. After another heat-
ing in the muffle furnace, the residue still was not completely
white.

After repeated nitric acid oxidations, a white water-and-HCl
residue was left. This was water washed in the hope that the trace
elements would be extracted. The residue was filtered off and dis-
carded and the solution diluted to 50 ml. The theoretical concen-
tration factor is 40:1.

2. Results

	Blank		Standard		Sample	
	Abs.	µg/l	Abs.	µg/l	Abs.	µg/l
Cobalt	0.538	0	0.123	100	0.082	68
Copper	0.014	0	0.039	100	0.092	230
Iron	0.085	0	0.053	100	0.0	0
Zinc	-	0	0.690	300	0.513	225

H. Lake Erie Water (May)

1. Preparation of the Sample

Two liters of the May composite of Lake Erie water were filtered through an 0.8 micron millipore filter and then passed through double ion exchange columns containing Dowex 50 and Amberlite 400. The effluent from the anion exchange resin was evaporated and adjusted to 25 ml. This should contain all the nickel at an 80:1 concentration. The columns were eluted with 10N HCl and the volume adjusted to 50 ml giving a 40:1 concentration factor.

2. Results

	Blank		Standard		Sample	
	Abs.	µg/l	Abs.	µg/l	Abs.	µg/l
Cobalt	0.550	0	0.130	100	0.032	28
Copper	0.012	0	0.080	200	0.079	200
Iron	0.077	0	0.400	500	0.131	160
Nickel	-	0	0.009	170	0.003	60
Zinc	-	0	0.570	250	0.830	350

I. Concentration of Trace Elements by Coprecipitation

1. Preparation of the Sample

One liter of the May Lake Michigan water was treated with 100 ml of 5% Na_2CO_3 and allowed to stand overnight. The pH was between 11 and 12. The resulting precipitate was filtered using a fine fritted glass filter. The residue was dissolved in 15 ml of 2N HCl and the beaker and filter were washed with several portions of high purity water. The volume was adjusted to 50.00 ml using high purity water. The concentration factor is 20:1.

2. Results

	Blank		Sample	
	Abs.	µg/l	Abs.	µg/l
Cobalt	0.540	0	0.538	0
Copper	0.007	0	0.010	24
Iron	0.072	0	neg.	-

V. SUMMARY

Spectrophotometric analytical procedures for trace elements in natural waters were developed for cobalt, copper, iron, manganese, nickel, and zinc. The procedures described were very satisfactory for cobalt, copper, iron, and zinc. The manganese procedure lacked the necessary sensitivity for trace work and some attempts were made to improve it. The nickel determination was very lengthy, not highly sensitive, and did not give reproducible results. A summary of the methods is given below.

INFORMATION ON THE DETERMINATION OF TRACE ELEMENTS

Element	Detection Limit ($\mu g/l$)	Limit for 10% Accuracy ($\mu g/l$)	Solvent	Wavelength Millimicrons
Co	50	100	H_2O	420
Cu	20	100	$CHCl_3$	435
Fe	10	30	isoamyl + ethyl alcohols	533
Mn	100	500	H_2O	525
Ni	50	100	H_2O	460
Zn	1	30	CCl_4	535

Various methods were tried for concentration of natural waters so that trace elements would be detectable. These included concentration by evaporation, by ion exchange through various resins and combinations

of resins, and by coprecipitation. The latter study was not completed.

Future work in this field could include investigation of procedures using a more sensitive spectrophotometer than the Spectronic 20, and the use of entirely new techniques involving atomic absorption or specific ion electrodes.